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PASSIVE CORROSION BEHAVIOR OF ALLOY 22 IN MULTI-IONIC AQUEOUS ENVIROMENTS

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ABSTRACT

In current waste packaging design, Alloy 22 (Ni-22Cr-13Mo-3W-3Fe) has been chosen as the candidate materials to fabricate a 2 cm outer layer of the high-level nuclear waste containers, as part of proposed geological repository at Yucca Mountain, Nevada. During the repository period, the container materials will be subject to the corrosion due to its exposure to the multi-ionic aqueous environments. Although Alloy 22 has demonstrated excellent corrosion resistance, but accumulation of small yearly corrosion rate for 10,000 or more years can be significant enough. The goal of this research is to seek alternative techniques to obtain a reasonably confident corrosion rate determination, since the conventional weight loss technique requires many years to achieve a detectable weight loss in Alloy 22 samples. This paper will discuss the latest experiment results in using potentiostatic technique to determine passive dissolution rates.

Key words: Passive dissolution, passive film, potentiostatic measurements, applied potentials, simulated acidic water (SAW), simulated concentrated water (SCW).

INTRODUCTION

Due to its excellent corrosion resistance, Alloy 22 (UNS No. N06022) has been chosen as the candidate material by the waste package design to fabricate the outer layer of the high level nuclear waste containers, as part of the proposed geological repository at Yucca Mountain, a federal land adjacent to the Nevada Test Site about 100 miles northwest of Las Vegas, Nevada. US Department of Energy (DOE) is required to use a performance assessment to demonstrate that there is a reasonable expectation that for 10,000 years following disposal, the waste packages maintain their structural integrity that prevents leaking of radioactive waste materials. Among the potential degradation modes for the engineering barrier system in the proposed repository, corrosion degradation of waste package materials has been under intensive study for the past two decades. The general consents are that the waste package will be in contact with aqueous

environments after initial dry period. The aqueous corrosion will be the predominant degradation mode throughout the repository lifetime.

The conventional method in weight loss measurement for corrosion studies is in its sixth year at the long-term corrosion test facility (LTCTF) at Lawrence Livermore National Laboratory ^[1]. Thus far, all weight loss data of Alloy 22 from LTCTF are extremely low (close to the detection limit of weighing devices) ^[2], and the information is not adequate to be used for modeling to predict the general corrosion of Alloy 22 throughout the repository lifetime. Alloy 22 shows strong passivity over a wide range of potentials in most aqueous environments. The general corrosion rate of Alloy 22 in relevant aqueous repository environments will be dictated by the dissolution rate of passive film on the surface. Therefore, the accurate determination of passive film dissolution rate can in turn provide a valuable alternative to the corrosion rate determination. This paper will summarize and discuss some of results from our recent electrochemical experiments in determining passive dissolution rate of Alloy 22 in simulated repository aqueous environments.

EXPERIMENT PROCEDURES

The alloy used in this study is wrought mill annealed Alloy 22, a Ni-Cr-Mo-W alloy. Table 1 lists the nominal chemical composition.

Table 1. Chemical composition of Alloy 22 (UNS No. N06022) given in weight percent.

Element	Mo	Cr	W	Fe	Co	C	Si	Mn	V	P	S	Ni
Discs specimens (Heat#: 2277-9-3203)	13.6	22.0	3.0	4.4	2.3	0.005	0.05	0.22	0.19	0.01	<0.01	Balance
Rod Specimens (Heat#: 2277-0-3251)	14.1	22.5	2.7	4.5	1.3	0.003	0.03	0.31	0.16	0.01	<0.01	Balance

The specimens used in electrochemical tests were metal discs with 15 mm in diameter and 3 mm in thickness. The disc specimens were placed in an ASTM G5 type flat specimen holder with an exposed area of around 0.75 cm². Rod specimens with 25.4 cm long and 0.625 cm in diameter were also used in corrosion potential monitoring. The disc specimens were wet polished with 600-grit SiC paper, then ultrasonically rinsed in distilled water. A three-electrode cell with a capacity of 1 liter was used for experimentation. About 900 ml of electrolyte was used in every test. A silver/silver chloride (Ag/AgCl) reference electrode was used for measuring and controlling the potential of working electrode. A standard reference potential of an Ag/AgCl electrode at 25°C in saturated KCl solution is 199 mV more positive than a standard hydrogen electrode. A solution bridge with a luggin probe was used to maintain an ionic conductive path between working electrode and reference electrode, while a cooling device was able to maintain the reference electrode to operate at near room temperature. A platinum (Pt) rod was used as a counter electrode. The electrochemical cell assembling was placed in a

temperature bath to achieve the desirable test temperatures. An Allihn condenser was used to prevent solution loss from heating. The test temperature was 90°C.

The test solutions used in this study were simulated acidified water (SAW) and simulated concentrated water (SCW). SCW is formulated to simulate evaporative process of ground water at the heated waste container surface, and it is approximately equivalent to 1000 times of concentration of J-13 water, a reference used to represent Yucca Mountain ground water chemistry [3]. SAW is similar to SCW, but acidified to pH 2.7. SAW is intended to simulate acidification of ground or pore water by the surface process of engineering components. Table 2 lists the core composition of SAW and SCW in comparison to J-13 water [4]. CO₂-free compressed air was used to purge the test solution for the tests under aerated condition, while N₂ was used for the tests under de-aerated condition. Gas purging began at least half hour before the specimen being placed in the solution.

Table 2. Chemical composition (in mg/l) of SAW, SCW and J-13 water.

Ion	SAW (pH 2.8)	SCW (pH 7.8)	J-13 (pH 7.4)
K ⁺	3400	3400	5.04
Na ⁺	40,900	40,900	45.8
Mg ²⁺	1000	<1	2.01
Ca ²⁺	1000	<1	13.0
F ⁻	0	1400	2.18
Cl ⁻	24,250	6700	7.14
NO ₃ ⁻	23,000	6400	8.78
SO ₄ ²⁻	38,600	16,700	18.4
HCO ₃ ⁻	0	70,000	128.9
SiO ₃ ²⁻ /Si	~40	~40	61

Potentiostatic measurement was carried out by applying a constant potential for one day (22 hours). For the tests in SAW, two applied potentials of +0.1 and +0.4 V (verse Ag/AgCl) were chosen, while an applied potential of +0.1 V (Ag/AgCl) was used in SCW tests. Applied potentials of 0.1 V and 0.4 V (Ag/AgCl) in aerated SAW at 90°C are over-potentials of approximately 200 mV and 500 mV, respectively, while applied potential of +0.1 V (Ag/AgCl) in aerated SCW at 90°C is approximately a over-potential of 400 mV. The anodic current density recorded at the end of potentiostatic test is used to represent the dissolution rate. The rate in current density can be converted to penetration rate (PR) based on the calculation of:

$$PR = [K * (EW) / \rho] * i$$

Where

PR is given in $\mu\text{m/yr}$, i is current density in $\mu\text{A/cm}^2$

$K = 3.27$, mm g/ $\mu\text{A cm yr}$

EW (equivalent weight) = 23.28 for Alloy 22 (ASTM G102)

$\rho = 8.69$, g/cm³ for Alloy 22

Potentiodynamic measurement was carried out at 2 scan rates: a commonly used scan rate of 0.167 mV/second and a much slower scan rate of 0.0025 mV/second.

RESULTS AND DISCUSSION

Figure 1 shows the corrosion potential E_{corr} of Alloy 22 in 90°C SAW. An increase of 500 mV in corrosion potential was observed within 6 weeks, and the corrosion potential remained at the elevated level thereafter. Although the corrosion potential approached the solution redox potential that was measured on the Pt electrode, it did not exceed the solution redox potential. No parallel measurement was done in SCW, however the ennoblement was also observed in the specimens from the long-term test facility. The corrosion potential of Alloy 22 after 4 ½-years exposure reached 390 mV (Ag/AgCl) in 90°C SAW, and 50 mV (Ag/AgCl) in 90°C SCW. In either case, the corrosion potential drifting was still within the passive region. Figures 2 and 3 show the typical anodic polarization curves for Alloy 22 at 90°C in SAW and SCW, respectively. Based on the anodic polarization results, Alloy 22 has a critical potential of 610 mV (Ag/AgCl) in SAW at 90°C, and a critical potential of 160 mV (Ag/AgCl) in SCW at 90°C. Critical potential is defined as the potential above which significant increase current density is observed. In SCW, an anodic peak was observed at 300 mV, above which a pseudo secondary passive region was observed.

Figures 4 and 5 show the current density vs time (i - T) curves recorded from the potentiostatic measurements at 90°C in SAW with applied potential of 0.1 V and 0.4 V (Ag/AgCl), respectively. Figure 6 shows the potentiostatic test results in SCW at 90°C. All curves show an attenuating pattern in the anodic dissolution rate, it indicates that passive dissolution decreased with increasing thickness and stability of passive film. A curve fitting technique was used to extract the mathematic behavior of the current density in time. All decaying curves followed a power function of:

$$\text{Rate} = A * (\text{Time})^{-n}$$

Where n is the attenuation factor, while A is the amplitude with same unit as the rate, either in $\mu\text{A}/\text{cm}^2$ or $\mu\text{m}/\text{year}$. The higher the absolute value of n , the more rapid the current decay. Table 3 summarizes the passive dissolution rate, as well as n and A values, determined by potentiostatic tests.

Table 3. Results of passive dissolution rate, constants A and $-n$ determined after 1-day potentiostatic measurement. Both dissolution rate and constant A have a unit in $\mu\text{m}/\text{year}$, while constant n has no unit.

	0.1 V applied potential in SAW		0.4 V applied potential in SAW		0.1 V applied potential in SCW	
	Aerated	De-aerated	Aerated	De-aerated	Aerated	De-aerated
Rate after 1 day ($\mu\text{m}/\text{year}$)	0.73	0.46	1.45	0.71	1.66	1.25

A ($\mu\text{m}/\text{year}$)	112.13	111.25	20.67	63.07	56.24	106.00
-n	-0.4555	-0.4967	-0.2477	-0.4121	-0.3181	-0.4034
R ²	0.9524	0.9487	0.7287	0.9082	0.9165	0.9395

The results indicate that passive dissolution rate in SCW (pH 7.8) was noticeably higher than the rate in more acidic SAW (pH 2.78). A similar observation of higher corrosion rate in SCW was also made in weight loss measurements from the specimens exposed in LTCTF. Presently, only limited data ^[5] in surface analysis is available to characterize the passive film and understand the passive phenomenon of Alloy 22. One speculation is that the stability of Mo -oxide plays a very important role in the overall stability of passive film. According to Pourbaix diagrams ^[6], Mo-oxide is not stable at neutral and alkaline environments, while Mo-oxide is more stable in acidic environments. For Alloy 22 in SAW, a stable Mo/Cr oxide in addition to the depletion of Ni in the passive film could be the cause in creating a Cr-rich film composition that drives up the corrosion potential, and reduces the dissolution rate.

The data from both SAW and SCW indicates that the anodic dissolution rate was slightly higher when the solution was fully aerated. Some argue that the increase in anodic dissolution rate is due to the increased activity of oxygen reduction in aerated environments. However, the contribution of oxygen reduction is to generate a cathodic current, which in fact should decrease the net current and decrease the anodic dissolution rate. It is not clear presently what is the mechanism behind this oxygen effect.

From all tests included in this study, no localized corrosion was observed in Alloy 22 at all potentials. By applying a 0.4 V (Ag/AgCl) to Alloy 22 in SAW at 90°C for as long as one month, no localized corrosion was observed. Potentiostatic technique is useful in confirming the susceptibility of localized corrosions as function of applied potentials. If a localized corrosion were initiated during a potentiostatic test, an increase in current density would have been observed.

Table 4 tabulates the extrapolated passive dissolution rate by using the experiment results from Table 3. It certainly is disputable for its validity of using an extrapolated data for projecting the passive dissolution rate in years away. However, there is no other undisputable method available either.

Table 4. The extrapolated passive dissolution rates, in $\mu\text{m}/\text{year}$.

	0.1 V applied potential in SAW		0.4 V applied potential in SAW		0.1 V applied potential in SCW	
	Aerated	De-aerated	Aerated	De-aerated	Aerated	De-aerated
After 1 week	0.2607	0.1495	0.7642	0.2613	0.8145	0.4932

After 1 month	0.1344	0.0726	0.5329	0.1435	0.5127	0.2742
After 1 year	0.0431	0.0210	0.2870	0.0512	0.2316	0.1001
After 2 years	0.0314	0.0149	0.2417	0.0385	0.1857	0.0757
After 5 years	0.0212	0.0097	0.1953	0.0270	0.1413	0.0535
After 10 years	0.0151	0.0067	0.1623	0.0198	0.1113	0.0395

The measured and projected passive dissolution rates are still much higher than the weight loss observed from the 2-year immersion tests. One very important difference is in the passive film evolution process. For the immersion test specimen, the ennoblement involves the anodic and cathodic processes within a same metal surface. With a given anode site, there should also be an equivalent cathode site. Therefore, anodic oxidation is always supplemented and same time constrained by the cathodic reduction. However, for a polarization technique, anodic oxidation can be supported by an external power source, equivalent to an infinitive cathodic support. It is a scenario much more similar to the localized corrosion. Therefore, the dissolution rate determined by potentiostatic technique will always be greater than the weight loss rate from an immersion test. However, at any given potential, potentiostatic measurement can provide an accurate determination of maximum dissolution rate per unit surface.

Figure 7 shows the anodic polarization curve (curve in the left) generated by the potentiodynamic polarization technique at a very slow potential scan rate (0.0025 mV/second), compared to the curve (curve in the right) generated with a normal scan rate of 0.167 mV/second. With the slower scan rate, the passive current density was approximately 10 times lower than the one generated by the faster scan rate. The passive current density at 0.4 V (Ag/AgCl) was 6.5×10^{-8} A/cm², or a passive dissolution rate of 0.6 μ m/year, which was slightly lower than the value measured by potentiostatic technique. It appears that the potentiodynamic polarization technique can be another valid option as an alternative method in passive dissolution determination. However, the key is to find a scan rate low enough. It is well known that scan rate has great deal of influence in polarization behavior resulted from a potentiodynamic polarization measurement [7]. Slower scan rate ensure the potential scanning process close to steady state. The slow progression on the potential may create a passive surface similar to the surface with natural ennoblement process, which was illustrated in Figure 1.

CONCLUSION

1. At a constant applied potential, the passive dissolution rate of Alloy 22 was higher in SCW than in SAW, possibly due to the lack of Mo-oxide stability in SCW.
2. Slightly higher passive dissolution rates were observed in aerated SAW and SCW than in de-aerated solutions.

3. Potentiostatic measurement gave a higher dissolution rate than weight loss in immersion test. The immersion test specimen has limited cathodic reaction available to support any anodic dissolution. However, potentiostatic measurement determines the maximum anodic dissolution rate at a given potential.
4. Potentiodynamic technique can be a valid alternative in the determination of passive dissolution rate, when the potential scan rate is adequately low.

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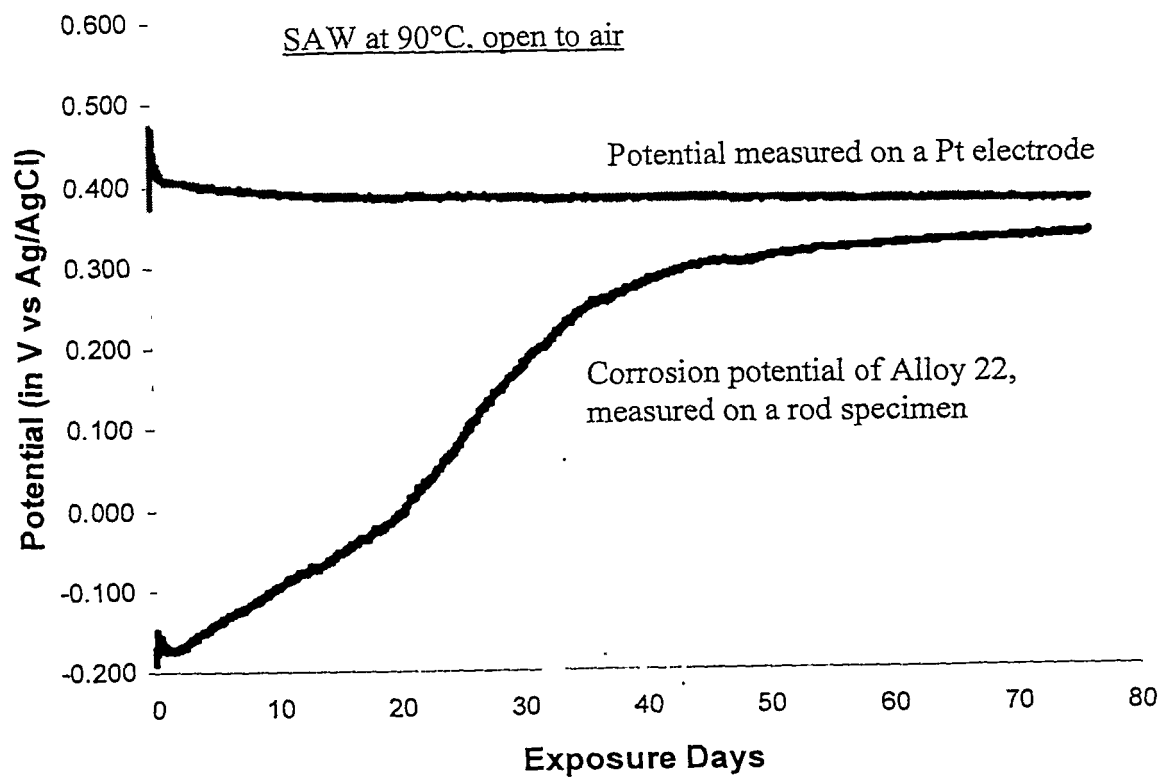


Figure 1. Corrosion potential of Alloy 22 increased with time in SAW at 90°C.

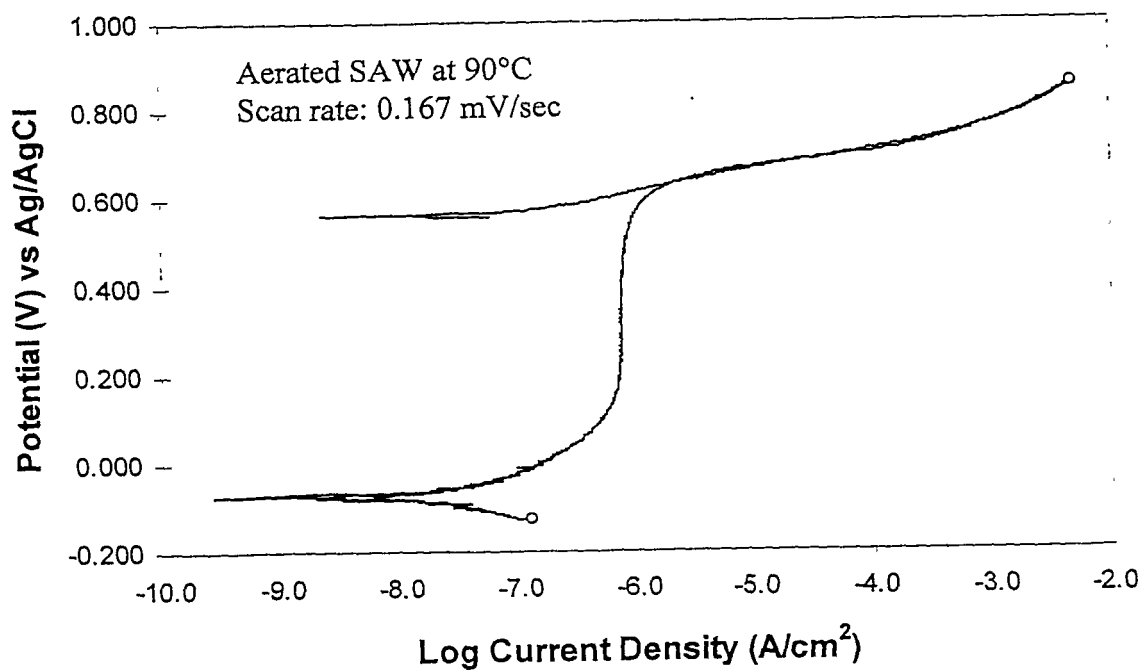


Figure 2. The anodic polarization curve for Alloy 22 in 90°C SAW.

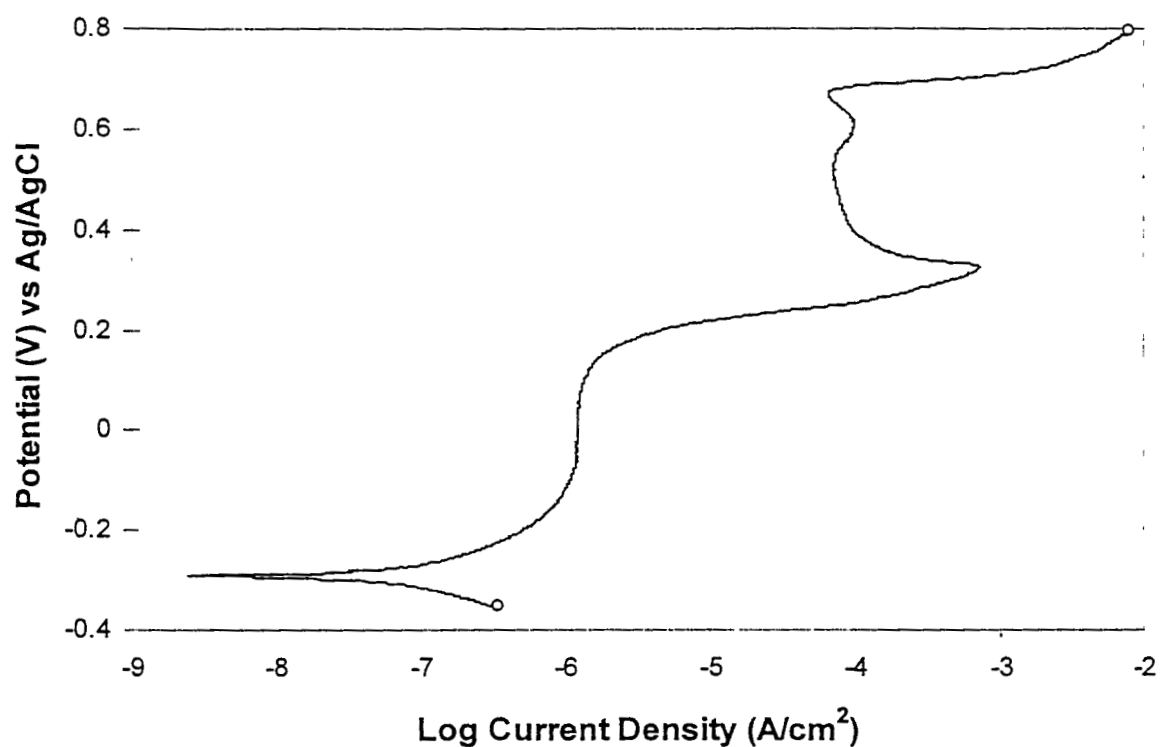


Figure 3. The anodic polarization curve for Alloy 22 in 90°C SCW.

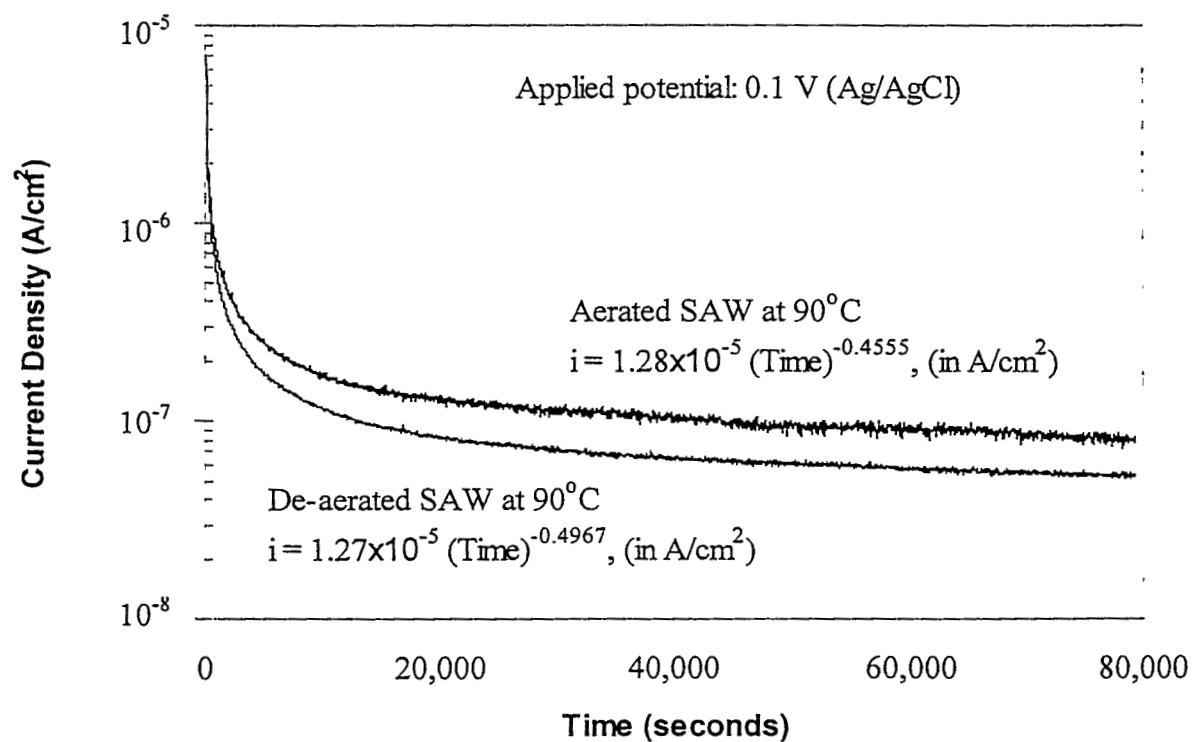


Figure 4. Results of potentiostatic tests with 0.1 V (Ag/AgCl) applied potential in SAW.

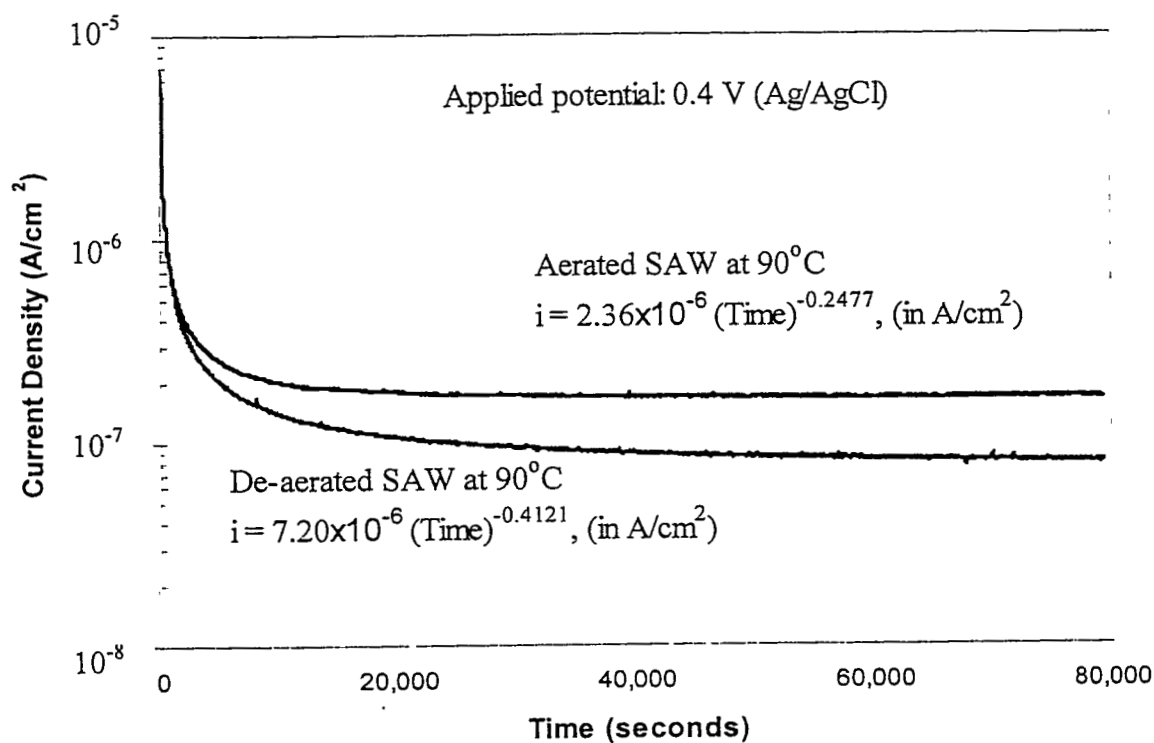


Figure 5. Results of potentiostatic tests with 0.4 V (Ag/AgCl) applied potential in SAW.

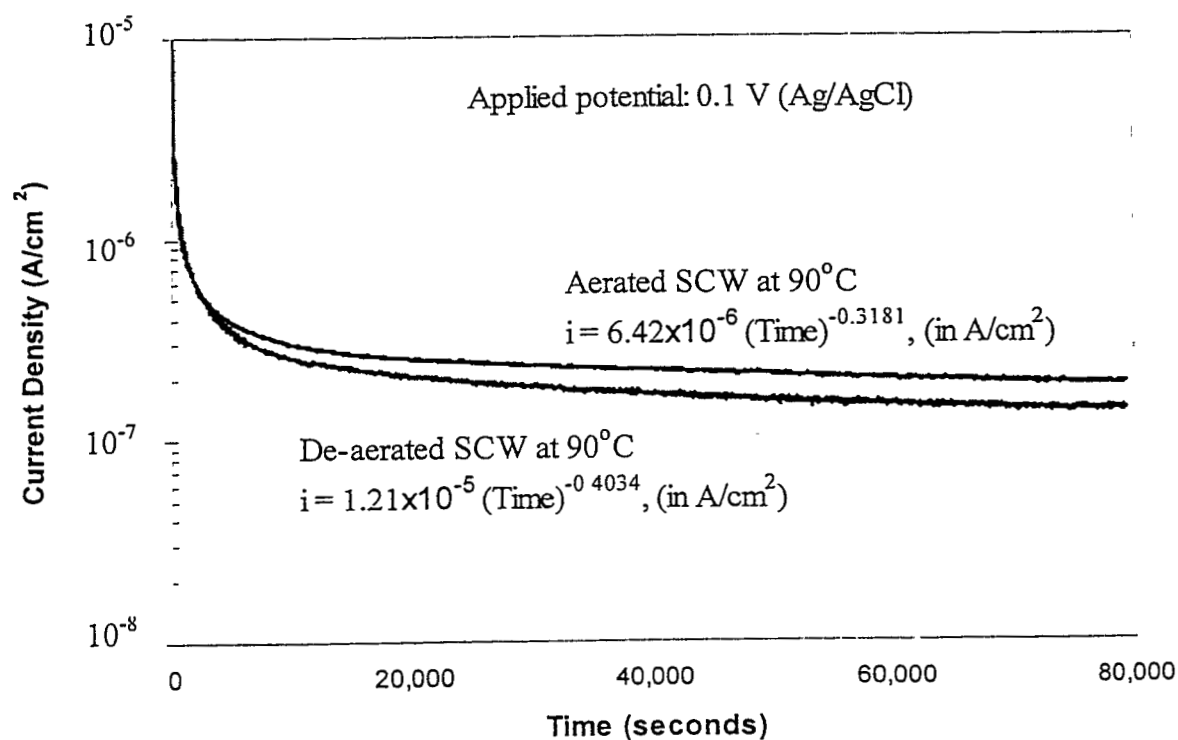


Figure 6. Results of potentiostatic tests with 0.1 V (Ag/AgCl) applied potential in SCW.

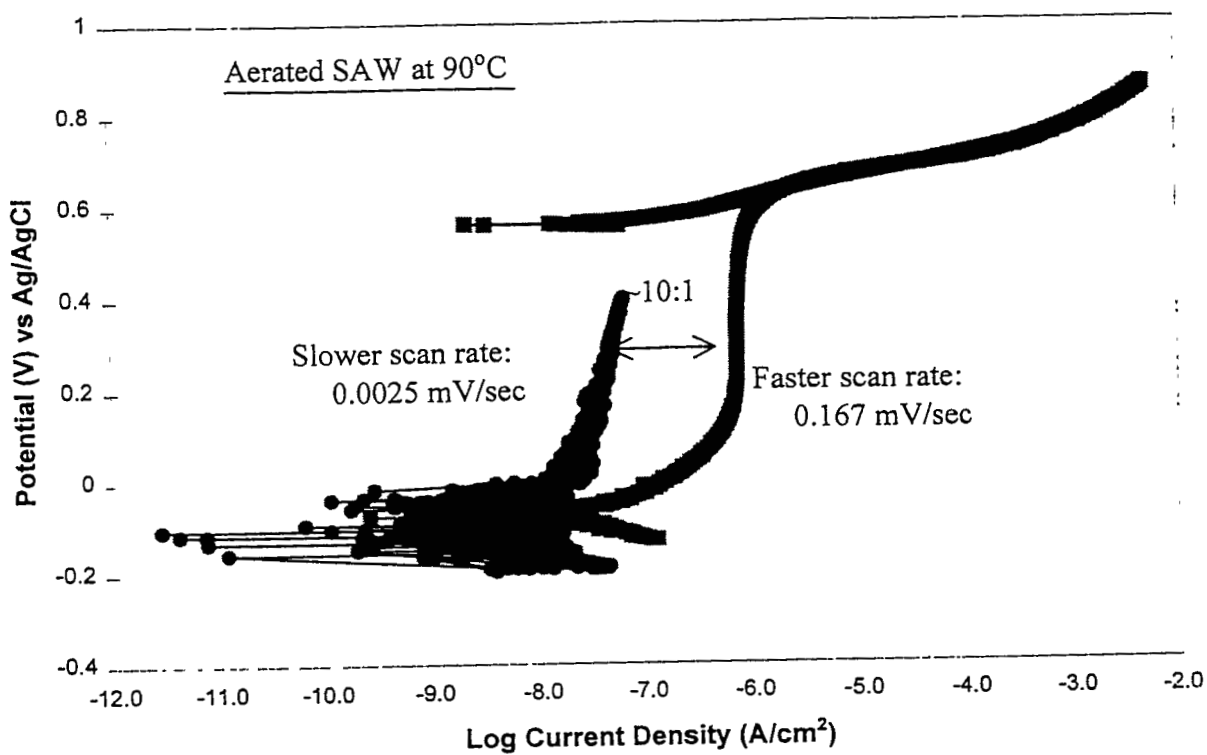


Figure 7. Results of potentiodynamic polarization technique to determine passive dissolution rates of Alloy 22 in aerated SAW at 90C.